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(54) **Process for the preparation of concentrated solutions of azo dyestuffs and solutions thus obtained**

(57) The invention provides a process for the preparation of a concentrated solution of an azo dyestuff from a diazotisable amine and a coupling component by diazotisation and coupling in the presence of water and of at least one water miscible solvent in which the diazotisation is effected by sodium nitrite in the presence of sulphuric acid, and the sodium sulphate formed is eliminated by filtration.

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SPECIFICATION

Process for th pr parati n of concentrated s lutions f az dy stuffs and s lutions thus obtained

The present invention relates to a process for the preparation of azo dyestuffs directly in the form of stable concentrated solutions and the solutions thus obtained.

Water-soluble anionic dyestuffs are generally sold and used in the form of powders comprising a more or less large proportion of inorganic salts. Some advantages, but also numerous disadvantages, are linked to this method of presentation. The principal advantage resides in the great stability on storage of these products; in particular no modifications are observed during their keeping, even at temperatures below 0°C, which enables them to be stored in all seasons in unheated locations.

On the contrary, it is known that powdered dyestuffs have a marked tendency to give off dusts when they are handled. Attempts have been made to remedy this disadvantage by different processes. By the addition of oils or hydroscopic liquids the amount of dust given off is effectively reduced; on the other hand, putting the dyestuffs into solution becomes more difficult. An attempt has also been made to make the dyestuffs less liable to form dusts by converting them into granules. Since the dyestuffs are then in a very compact form, it becomes very difficult to dissolve them, in particular with dyestuffs which are only slightly soluble in water. This is the case with the dyes with which the present process is concerned, when they are presented in the form of powder.

The present invention relates to a process for the preparation of stable concentrated solutions of water-soluble azo dyes and more particularly those described in the Colour Index under the names of Acid Orange 7 and Acid Orange 8. The concentrated solutions obtained according to the present process contain from 40 to 65% of dyestuff with regard to the total weight of the solution.

Solutions of azo dyestuffs have already been proposed. U.S. Patents Nos. 3,898,033, 4,019,858, 3,551,088, 3,681,320, 3,986,827, 4,082,742, 4,043,752, 4,063,880, and French Patents Nos. 2,197,951, 2,216,324 and 2,109,806 describe solutions the concentration of which does not exceed 25% of dy stuff. Other Pat nts, for exampl German Patents Nos. 2,629,673 and 2,629,674 as well as British Patent No. 1,355,437, describ solutions of which the concentration can attain 40%, but their pr parati n involves the dry dyestuffs. In practice, it is necessary to pr pare the dyestuff in wat r, separate it by filtration, dry it, dissolve it in th solvent or solvents necessary and eliminate th ins luble parts by filtration. This process is long and necessitates numerous op rations and is ther fore onerous. Other patents describe analogous processes of preparation. This is the case with French Patents Nos. 2,193,065, 2,316,296, German Patents Nos. 2,061,760 and 2,341,293 and Belgian Patent No. 828,876. In some cases the use of the moist paste of the dyestuff may be envisaged, which would constitute a certain advantage if it were not necessary to prepare the free acid of the dyestuff as in Belgian Patent No. 631,379. In fact, it is often difficult to obtain the free acid of a sulphonated dyestuff and the suspensions which it entails are generally difficult to filter.

French Patent No. 2,110,324 refers to solutions comprising up to 75% by weight of the dyestuff. Nevertheless, and this also results from the teaching of French Patent No. 2,174,161, really concentrated solutions can only be obtained if the diazotisation is effected by means of alkyl nitrites, nitrous anhydride or mixtures of nitrogen oxide and air. In fact, it is evident from Examples No. 10, 11, 15 to 17 of French Patent No. 2,110,324 that the use of sodium nitrite for the diazotisation of the amines taking part in the constitution of the dyestuffs leads to more dilute solutions. In effect the weight of solution obtained for one part of β-naphthol is 9.136 parts in Example 10 and 8.819 parts in Example 11, Examples which use sodium nitrite as diazotising agent, although this weight is only 6.16 parts in Examples 15 to 17. But the use of alkyl nitrites necessitates their preparation and their separation which makes the production of the solutions of dyestuff longer, more complicated and more onerous.

However, we have now found that it is possible to obtain solution which are at least as concentrated, but in a much simpler way by using sodium nitrite as the diazotising agent.

The present invention therefore relates to a process for the preparation of solutions of azo dyestuffs from diazotisable amines and coupling components in which the diazotisation is effected in the presence of water and at least one water miscible solvent and that the diazo compound obtained is coupled with the coupling component in a mixture containing solvents and water, the diazotisation being effected by means of sodium nitrite in the presence of sulphuric acid and the sodium sulphate formed being eliminated from the solution by filtration.

Examples of solvents which may be used in th coupling medium ar th thers deriv d from ethyleneglycol. As solvents for the coupling medium may be mentioned the ethanolamines. The percentage relation of water-solvent may vary for example from 10/90 to 70/30. It is surprising to find that the sodium sulphat formed is totally or almost t tally

precipitated and that the dyestuff obtained remains completely in solution.

By this process s lutions can b btained comprising

- 40 to 65% of dyestuff
- 10 to 40% of a mixture of solvents comprising:
  - 25 to 75% of monoethyleneglycol
  - 75 to 25% of the methyl or ethyl ether of monoethyleneglycol .
- 0 to 30% of a mixture comprising:
  - 0 to 5% of monoethanolamine
  - 0 to 5% of diethanolamine
  - 100 to 90% of triethanolamine
- 10 to 30% water and
- less than 2% of sodium sulphate.

The process according to the present invention is applicable to the preparation of azo dyestuffs, more particularly to the preparation of the dyestuffs known under the names of Acid Orange 7 (sodium salt of [4-sulphobenzene]-<1 azo 1>-[2-hydroxy-naphthalene]) and Acid Orange 8 (sodium salt of [4-sulpho-2-methylbenzene]-<1 azo 1>-[2-hydroxy-naphthalene]) as well as their mixture.

The solutions obtained are characterised by complete miscibility with water and a great stability on storage, even at very low temperatures. Neither crystallization nor decomposition of the disclosed dyestuffs is observed even after several months storage at 20°C.

The invention is illustrated by the following Examples in which the parts are by weight.

EXAMPLE 1

173 parts of sulphanilic acid were mixed with 50 parts of monoethylene-glycol, 50 parts of the methyl ether of monoethylene glycol, 50 parts of water, 100 parts of ice and 53 parts of 94% sulphuric acid. Then 70 parts of sodium nitrite were added in a period of 30 minutes. The mixture was left to react for 10 minutes until it was no longer possible to detect sulphanilic acid and 144 parts of β-naphthol were added in a period of 30 minutes, then gradually over a period of 1 hour 210 parts of an industrial mixture containing 96% of triethanolamine, 2% of diethanolamine and 2% of monoethanolamine were added. The mixture was left to react again for 30 minutes and then the sodium sulphate was separated by filtration. 772 parts of a solution containing 58.2% of the triethanolamine salt of the dyestuff Acid Orange 7 were obtained. By the addition to this solution of 23 parts of water one obtains 795 parts of a solution at a concentration such that 100 parts of the solution ar equival nt to 70 parts of th commercial dyestuff in the form of powder.

This solution is prefectly stable on storage. Aft r a period of storage of one month at −20°C, it is suffici nt to reheat to 0°C in order to obtain a solution identical with the initial pr duct and not pr senting any product of crystallisation. The w ight of the solution p r part of β-naphthol is 5.52 parts. The solution contains l ss than 1% of mineral salts.

EXAMPLE 2

If the operation is as in Example 1 but with 150 parts of the mixture of alkanolamines instead of 210 parts, the coupling lasts about 6 hours instead of 30 minutes. After separation of the sodium sulphate by filtration at 40°C, 720 parts of a solution containing 62.4% of dyestuff were obtained. By the addition of water the concentration of the solution was regulated to the desired value.

EXAMPLE 3

187 parts of 2-amino-toluene-5-sulphonic acid were mixed with 200 parts of monoethylene-glycol and 200 parts of the methyl ether of monoethylene-glycol. 100 parts of ice were added and then 53 parts of 94% sulphuric acid. 70 parts of sodium nitrite were then added in a period of 30 minutes. The mixture was left to react until the non-diazotised amine could no longer be detected. This suspension was then poured in a period of 20 minutes on a solution at 20°C of 144 parts of β-naphthol in 120 parts of technical triethanol-amine containing 2% of diethanolamine and 2% of monoethanol-amine. When the coupling was finished, the sodium sulphate was separated by filtration. 950 parts of a solution containing 48% of dyestuff were obtained. By the addition of water the concentration was regulated to the desired value. The solution was perfectly stable on storage. It contains less than 1% of mineral salts.

EXAMPLE 4

If instead of using 200 parts of ethylene glycol and 200 parts of the methyl ether of ethylene-glycol, 100 parts of the first and 300 parts of the second are used, or again 300 parts of the first and 100 parts of the second, solutions showing the same characteristics are obtained.

EXAMPLE 5

The diazo compound was prepared from 173 parts of sulphanilic acid according to the information in Example 1, then the suspension obtained was poured in a period of 30 minutes into a solution of 144 parts of β-naphthol in 210 parts of triethanolamine. After filtration the same solution was obtained as in Example 1.

EXAMPLE 6

If in Example 3 the 187 parts of 2-amino-toluene-5-sulphonic acid are replaced by 168.3 parts of the same product and 17.3 parts of sulphanilic acid, a solution is obtained which contains a mixture of 90% of the dyestuff Acid Orange 8 and 10% of the dyestuff Acid Orange 7.

EXAMPLE 7

187 parts of 2-amino-tolu n -5-sulphonic acid, 100 parts of monoethylen -glycol, 100 parts of the methyl ether of monoethylene-glycol, 100 parts of ice and 70 parts of sodium nitrite were mixed. 53 parts of 94% sulphuric acid were added in a period of 15 minutes and the diazotisation reaction was allowed to continue until diazotisable amine could no longer be detected. 144 parts of β-naphthol were added in a period of 30 minutes and then, gradually over a period of one hour, 210 parts of triethanol-amine (industrial product). The mixture was left to react for 30 minutes, then heated to 40°C and the sodium sulphate was separated by filtration. 810 parts of a solution containing 57% of the dyestuff Acid Orange 8 were obtained.

EXAMPLE 8

173 parts of sulphanilic acid were mixed with 40 parts of monoethylene-glycol, 40 parts of the methyl ether of monoethylene-glycol and 120 parts of water. Gradually over a period of one hour 70 parts of sodium nitrite were added and then in one hour 53 parts of 94% sulphuric acid. The diazotisation was allowed to finish and then 144 parts of β-naphthol were added. 180 parts of pure triethanolamine or of the same mixture as in Example 1 were run in in a period of one hour. The mixture was allowed to react for 30 minutes, heated to 60°C and the sodium sulphate was separated by filtration. 710 parts of a solution containing about 62% of dyestuff were obtained the concentration of which was regulated to a value such that 140 parts of the solution corresponded to 100 parts of the commercial product powder. This operation was effected either by the addition of water, monoethylene-glycol, the methyl ether of monoethylene-glycol, or a mixture of two of these products, one of them being water.

CLAIMS

1. Process for the preparation of a concentrated solution of an azo dyestuff from a diazotisable amine and a coupling component by diazotisation and coupling in the presence of water and of at least one water miscible solvent in which the diazotisation is effected by sodium nitrite in the presence of sulphuric acid, and the sodium sulphate formed is eliminated by filtration.

2. Process according to claim 1, in which the diazotisation is effected in a mixture of water, monoethylene glycol and the methyl or ethyl ether of monoethylene glycol.

3. Process according to claim 1 or 2, in which the coupling is effected in the presence of triethanolamine alone or a mixture of mono-, di- and triethanolamine.

4. Proc ss according to any of claims 1 to 3, in which the coupling component is β-naphthol.

5. Process according to any of claims 1 to 4, in which the diazotisable amin is sulphanilic acid.

6. Process according to any of claims 1 to 4, in which the diazotisable amine is 2-amino-tolune-5-sulphonic acid.

7. Process according to any of claims 1 to 4, in which the diazotisable amine is a mixture of sulphanilic acid and 2-amino-tolune-5-sulphonic acid.

8. Process for the preparation of a solution of an azo dyestuff substantially as herein described with reference to and as illustrated in any of the Examples.

9. Solution obtained according to the process of any of claims 1 to 8, comprising
- 40 to 65% of dyestuff
- 10 to 40% of a mixture of 25 to 75% of monoethylene glycol 75 to 25% of the methyl or ethyl ether of monoethylene glycol
- 0 to 30% of a mixture of
  0 to 5% of monoethanolamine
  0 to 5% of diethanolamine
  100 to 90% of triethanolamine
- 10 to 30% of water and
- less than 2% of sodium sulphate

10. Solution according to claim 9, in which the dyestuff is Acid Orange 7.

11. Solution according to claim 9, in which the dyestuff is Acid Orange 8.

12. Solution according to claim 8, in which the dyestuff is a mixture of Acid Orange 7 and Acid Orange 8.

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